

NHL SEP 21

(12) UK Patent Application (19) GB (11) 2 264 706 (13) A
(43) Date of A publication 08.09.1993

<p>(21) Application No 9303812.3</p> <p>(22) Date of filing 25.02.1993</p> <p>(30) Priority data (31) 4207059 (32) 06.03.1992 (33) DE</p>	<p>(51) INT CL⁵ C03B 5/225</p> <p>(52) UK CL (Edition L) C1M MDD</p> <p>(56) Documents cited None</p> <p>(58) Field of search UK CL (Edition L) C1M MDD INT CL⁵ C03B Online database: WPI</p>
<p>(71) Applicant Carl-Zeiss Stiftung (Incorporated in the Federal Republic of Germany) Schott Glaswerke, Hattenbergstr 10, 6500 Mainz, Federal Republic of Germany</p> <p>(72) Inventors Friedrich G K Baucke Thomas Pfeiffer</p> <p>(74) Agent and/or Address for Service Marks & Clerk Alpha Tower, Suffolk Street, Queensway, Birmingham, B1 1TT, United Kingdom</p>	

AN

(54) Process for refining oxide melts

(57) An oxide glass melt 10 in a tank 20 is refined by applying a voltage across a refining electrode 30 and a counter electrode 40 so as to generate oxygen and a refining gas electrochemically.

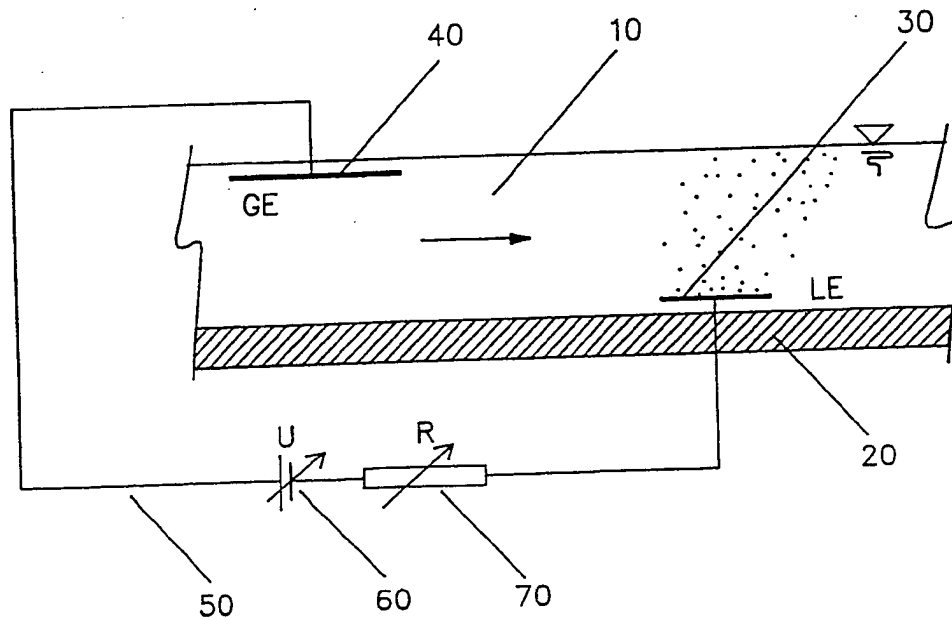


Fig.1

Ø Ljungman
24 P 1431 EP

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

GB 2 264 706 A

Process for Refining Oxide Melts

The invention relates to a process for refining oxide melts, particularly glass melts.

In relation to melts, refining is understood to mean the removal of gas bubbles from the melt. In order to achieve maximum freedom from unwanted gases and bubbles, thorough mixing and degassing of the molten mixture, for example, the glass, is required.

The behaviour of gases and bubbles in a glass melt and the removal thereof is described, for example, in "Glastechnische Fabrikationsfehler", published by H. Jebesen-Marwedel and R. Brückner, 3rd edition, 1980, Springer-Verlag, on pages 195 et seq.

Generally speaking, two different refining processes are known, which differ essentially in the nature and manner of refining gas generation.

In mechanical refining, water vapour, oxygen, nitrogen or simply air are forced in through openings in the bottom of the melting unit. In this so-called bubbling process, the melt then becomes thinner as a result of a further increase in temperature, and the gas bubbles can rise more easily to the surface. This stage of the process is also known as "bubble removal". In the bubbling process, freedom from unwanted gases is often improved by agitators. As the bubble size of the refining gases forced in is generally too large, however, and the gas bubbles rise too quickly, the extremely high degrees of freedom from unwanted gases required for melting optical glasses, for example, are achieved only with great difficulty, even by agitator support.

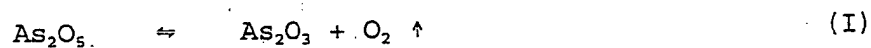
Chemical refining processes are used most frequently. Their principle lies in the fact that compounds that decompose and dissociate gases, or compounds that are volatile at relatively high temperatures, or compounds that liberate gases in an equilibrium reaction at relatively high temperatures are added to the melt.

Sodium sulphate (Glauber's salt), for example, belongs to the first group of compounds, which cleaves sulphur dioxide and oxygen at about 1,200 °C and is preferred as a cheap raw material for refining mass-produced glasses.

The compounds that are volatile at high temperatures because of their vapour pressure and are effective as a result include, inter alia, NaCl or certain fluorides.

Finally, the last group of substances includes the so-called redox refining agents such as, for example, arsenic oxide, antimony oxide or cerium oxide etc. In this by far the most frequently used process in practice, polyvalent ions which may occur in at least two oxidation states are used as redox refining agents, which ions are in a temperature-dependent equilibrium with one another, a gas, mostly oxygen, being liberated at high temperatures.

The redox equilibrium of the substance dissolved in the melt can be represented by the equation (I), taking arsenic oxide as an example



The equilibrium constant K for (I) may be formulated as in equation (II):

$$K(T) = \frac{a_{\text{As}_2\text{O}_3} \cdot P_{\text{O}_2}^*}{a_{\text{As}_2\text{O}_5}} \quad (\text{II})$$

In this equation, $a_{\text{As}_2\text{O}_3}$ and $a_{\text{As}_2\text{O}_5}$ mean the activities of arsenic trioxide and arsenic pentoxide, and $P_{\text{O}_2}^*$ means the fugacity of the oxygen.

The equilibrium constant K is highly temperature-dependent, and the defined oxygen fugacity $P_{\text{O}_2}^*$ can be adjusted by means of the temperature and the activities of the oxidic arsenic compounds.

Both in mechanical and chemical refining, essentially three refining effects may be distinguished:

- 1) a primary refining effect due to the spontaneous formation or introduction of gas bubbles, preferably oxygen bubbles, during the use of redox refining agents, whereby the unwanted gases dissolved in the melt, for example CO_2 , N_2 , H_2O , NO , NO_2 and others, diffuse into the gas bubbles. The gas bubbles thereby become inflated, and the inflated gas bubbles rise upwards more quickly, eventually leaving the melt;
- 2) a secondary refining effect in which the reverse process to the one described under 1) takes place, namely the diffusion of gases, for example oxygen, out of the redox equilibrium into unwanted gas bubbles present, so that said bubbles become inflated and receive an increased uplift and

- 3) a so-called resorption effect in which inflated bubbles of, for example, oxygen, produced according to 1) or 2) and still present in the melt when the temperature is reduced dissolve, for example, in the case of the redox equilibrium (I) as a result of the equilibrium being shifted to the side of the starting product.

A common feature of all chemical refining processes is that chemicals which are harmful to the environment, or at least not environmentally acceptable, are added to the melts. In addition, volatilisation refining agents, fluorides, may be mentioned for example, or arsenic or antimony oxides which act as redox refining agents. Already, certain substances can be used only on a very restricted scale now (fluorides, arsenic oxide) or in the near future (antimony oxide), and there are plans to prohibit their use altogether. Alternative redox refining agents, for example, cerium oxides, are relatively expensive substitutes.

Apart from mechanical and chemical refining, there have also been attempts to refine oxide melts by electrochemical means.

A process for refining oxide glass melts is known, for example, from US-A-3,775,081, in which the refining gas is generated in situ in the oxide melt in an electrochemical reaction. To this end, small quantities of molten metal are required on the bottom of a melting vessel in order to generate hydrogen gas in an electrochemical reaction from water vapour which is present in the glass melt or has diffused therein, which gas is claimed to serve as a refining gas for refining the melt.

The process described in US-A-3,775,081 is, however,

associated in various ways with considerable disadvantages. The process is restricted to gas-heated melting tanks, since water vapour can be made available in such quantity as is sufficient to generate the hydrogen refining gas only in tanks heated with gas or oil, but not in electrically heated melting tanks. The presence of a source of water vapour in the melt to be refined - whether the water vapour results from burning fuel or, another possibility, whether it is introduced - is extremely disadvantageous in this connection because the melt must, in principle, be kept free from water vapour for effective refining in order to avoid the "reboil effect" of the melt.

In addition, with the process according to US-A-3,775,081 there is the risk that concentrations of metal ions of polyvalent metals other than the desired concentrations will be obtained in the glass produced. This may be the consequence of a varying partial pressure of water vapour becoming lower during the course of refining, which leads to a shift in the redox equilibrium of polyvalent ions, such as the reduction of Fe^{2+} to Fe^{3+} . Moreover, the requirement that the metal for reducing the water vapour in the process according to US-A-3,775,081 must be present in the molten state in order to achieve a sufficient reactivity of the metal restricts the process - depending on the glass melt - to tin, lead, antimony or nickel as metal. The converse conclusion is, therefore, that not every glass melt can be refined in this way. Moreover, a whole series of glasses is excluded a priori from the use of the refining process of US-A-3,775,081, however, because there is a risk that the glass components will be reduced by the molten metal. The greatest disadvantage, however, is likely to lie in the use of hydrogen as refining gas. The gaseous hydrogen may react immediately with oxygen in an explosive manner on leaving the melt.

Apart from electrochemical refining, in which gas bubbles are generated in the glass melt for the refining thereof, it is also known, for example, from GB-A-1,128,561, that the formation of gas bubbles produced by electrochemical reactions can be prevented in glass melts that have already been refined. In this connection, GB-A-1,128,561 advocates keeping a glass melt in an electrically conducting tank under a non-oxidising atmosphere in order to avoid the renewed occurrence of gas bubbles after refining.

Although GB-A-1,128,561 describes a principle according to which the development of gas bubbles in the melt appears to be explainable, the conclusions with regard to refining are incorrect or wholly absent. In GB-A-1,128,561, a so-called platinum/glass (T_1)-glass (T_2)/platinum thermocell is described, the short circuit of which leads to oxygen bubble formation in the "reboil effect". Contrary to the stated principle, however, oxygen formation may occur not only at the higher temperature electrode but also at the lower temperature electrode (Baucke, Mücke in Journal of Non-Crystalline Solids 84 (1986), page 174 ff). Moreover, the stated principle has another error. This consists in that the development of oxygen at the higher temperature electrode does not yet lead to bubble formation that can be used for refining, only to oxygen formation. In order to form bubbles from oxygen that can be used for refining, the higher temperature must lie in the vicinity of the reboil temperature.

Moreover, no indication can be derived from the entire prior art concerning electrochemical refining processes as to how the kinetics of the refining reaction are to be controlled, or how the thermodynamics of the refining reaction can be mastered and used in a purposeful manner. In other words, no method is shown as to how the number

of bubbles and the size of the refining gas bubbles could be adjusted.

In comparison with the prior art described, the object of the invention is to provide a process for refining oxide melts which makes it possible to obtain melts with a high degree of freedom from unwanted gases and at the same time to dispense with the use of environmentally harmful refining chemicals, or at least markedly limit the use thereof. At the same time, the new process should be simple and cheap to carry out.

In particular, the disadvantages of the electrochemical refining process with hydrogen generated in situ should be avoided, whereby an electrochemical refining process should be specified with which both the kinetics and the thermodynamics of refining gas development can be controlled.

According to the invention, there is provided a process for refining an oxide melt, in which a refining gas is generated electrochemically in situ in the oxide melt, and wherein oxygen is generated electrolytically as the refining gas.

Advantageous process parameters and modifications are specified in the dependent patent claims.

The advantages of an electrochemical refining process consist essentially in that, in contrast to mechanical refining, the melting units do not have to be prepared specially for forcing in gases and in that the bubble size of the refining gas is easily adjustable. In contrast to the chemical refining method, particularly the redox refining method which had hitherto become established in practice, it is possible to dispense with the use of toxic or expensive redox chemicals, or the

amount thereof can be markedly reduced.

In the refining process according to the invention for oxide melts, particularly glass melts, at least two electrodes are provided which are both in contact at least partially with the oxide melt, for example, dip into the oxide melt and which are connected to each other by means of a power source so that, when a voltage is applied to one of the two electrodes, refining gas develops in the form of bubbles so that gaseous unwanted substances that are trapped in the melt are removed from the melt according to the primary and/or secondary refining effect described above.

The gas bubbles required to bring about the primary and secondary refining effect are, therefore, developed by electrolysis of the oxide melt at a refining electrode. In this process, oxygen develops in an electrochemical reaction according to equation (III).



In equation (III), (LE) stands for refining electrode and (GE) for counter-electrode. As the process according to equation (III) is a reaction in which the cathodic and anodic reactions have the same current intensity, the counter-electrode (GE) is installed preferably in a place in the melt that allows the presence of oxygen in the elemental gaseous form or the elemental dissolved form. In the case of oxide melts, this is preferably in the vicinity of the melt surface which is in contact with the atmosphere above the melt, in which case steps should be taken to ensure a sufficient oxygen content in the atmosphere above the melt.

It should be stated in this connection that preferably

oxygen is suitable for the electrochemical refining process described so far because both the melts and the atmosphere above the melt in the melting unit have sufficiently high activities or concentrations of O^{2-} ions or molecular oxygen in the dissolved or gaseous form. The use of other gases is, however, equally possible, but a sufficiently high activity of ions of said gas must be present in the melt, and the atmosphere outside the melt must have a sufficient concentration of said gaseous substance. Nevertheless, refining gas should usually be understood hereinafter to mean oxygen.

The refining electrode is provided preferably completely inside the oxide melt, whilst the counter-electrode, as explained already, dips partially into the oxide melt and is partially in contact with the atmosphere above the oxide melt, or is provided in the melt but near the melt surface.

In order to keep the oxygen bubbles developed at the refining electrode in contact for as long as possible with the melt and the unwanted gases for the diffusion of the unwanted gases into the O_2 bubbles and for diffusion for the unwanted gases, it is advisable to provide the refining electrode on the bottom of the melting unit, if possible, for example, on the bottom of the tank. It is also possible, *inter alia*, to construct the refining electrode as an integral component of the tank bottom or to design the tank bottom itself as the refining electrode.

The counter-electrode may also be provided in a separate melting unit. In order to carry out the process of the invention, it is merely necessary that the counter-electrode be in conductive connection with the refining electrode. This is done, for example, by means of connections, suitable connecting wires or lines. Of

course, it is also necessary in such a case that the melt in the separate melting unit be likewise in contact with the melt to be refined, for example, by means of a channel etc. By means of such an arrangement, however, advantageous thermostating and also control of the atmosphere and improved conditioning of the counter-electrode is possible.

In order to bring about the reaction according to equation (III), it is necessary to apply a voltage to the electrodes in conductive connection with one another. If a direct voltage is applied, the refining electrode is the anode, that is, to be connected to the positive pole and the counter-electrode is the cathode, that is, to be connected as the negative pole. When the direct voltage U of suitable magnitude is switched on, oxygen bubbles develop at the refining electrode according to the reaction of equation (III), the size of which bubbles depends on the voltage applied. It is thus quite possible to generate very small microbubbles to large bubbles, depending on the condition and the requirements of the melt to be refined.

Surprisingly, it has emerged, however, that an alternating voltage may also be used for refining. In this case, it is no longer possible to speak of anode or cathode, rather, the refining electrode is now the one at which the current density is greater. Current density is generally understood to mean the current per unit area. It is a measure of the rate at which ions can be discharged at electrodes. The refining electrode must, therefore, have a smaller surface area than the counter-electrode when an alternating voltage is applied, unless other parameters affecting the current density predominate or are even critical.

Apart from direct voltage and alternating voltage,

superimpositions thereof are also suitable as voltages, indeed, alternating voltage or superimposition of direct and alternating voltage are even advantageous because they offer greater protection against unwanted cathodic functions. The voltage is preferably adjustable, for example by means of a resistor.

In all cases, however, the amount and bubble size of the oxygen evolved at the refining electrode can be controlled and adjusted by means of certain parameters. Oxygen evolution depends, inter alia, on the type of voltage applied, the size and frequency of the voltage, the current density, the temperature and the composition of the melt etc. Taking these factors into account, however, all special systems can be optimised in a few tests by the man skilled in the art.

Moreover, the electrochemical refining process within the meaning of the invention may also be controlled electronically and, in particular, computer-controlled. Allowing for certain input values which may include, for example, melt composition, temperature of the melt or unwanted gas content of the melt, the above-mentioned parameters such as voltage and current density can be optimally adjusted.

In all events, it is generally necessary to make sure that the counter-electrode can come into contact with sufficient quantities of oxygen. If not enough oxygen is available, the melt will be electrolysed and silicon, for example, or other components of the melt will be precipitated onto the electrodes, which may lead to the ineffectiveness or destruction thereof. If all the parameters are coordinated, however, electrochemical refining permits so to speak an electrochemical pumping of oxygen from the atmosphere or of dissolved oxygen at the counter-electrode to oxygen in bubble form at the

refining electrode.

The special embodiments of the electrodes that may be used are usually known to the man skilled in the art. All substances that are, if possible, inert towards aggressive media and high temperatures have proved suitable as materials. These are, amongst others, noble metals such as platinum, noble metal alloys such as platinum-rhodium or platinum-iridium, conductive ceramics (not ionic, but electron-conducting or hole-conducting), SnO_2 ceramics, for example, in a tubular arrangement.

Using the electrochemical refining process according to the invention, it is possible to produce a very high degree of freedom from unwanted gases in the melt which is sufficient for most purposes. If it is necessary to increase further the freedom of the melt from unwanted gases, it is preferable to add to the melt about 1/10 of the quantity of a redox refining agent, the statement of quantity referring to the quantity of redox refining agent normally added to refine the melt without electrochemical refining. The resorption of the last residues of refining gas or residual refining bubbles is also thereby achieved. Of course, combinations of the electrochemical refining process according to the invention with other known refining processes are also possible.

An arrangement for carrying out the process of the invention is explained below in the figure.

The figure shows a diagrammatic representation of a melt 10 in a melting unit 20, for example, a tank, which is only suggested. One electrode, the refining electrode 30, is provided in the melt on the bottom of the tank 20, whilst the second electrode, the counter-electrode 40, is situated near the surface of the melt. Counter-electrode

40 and refining electrode 30 are linked together by means of a line 50, a power source 60 and an adjustable resistor 70. When a voltage is applied and the voltage and frequency adjusted, gas bubbles in the desired yield and size develop at the refining electrode with the smaller surface area so that refining of the melt is achieved. At the counter-electrode 40, molecular dissolved or free oxygen is converted to O^{2-} ions according to the reverse reaction of equation (III).

The invention is explained in more detail below on the basis of two embodiments given by way of example:

Example A:

In a Pt/10 Rh pot as vessel, which had a capacity of 2 l and could be heated inductively with 10 kHz, a glass was melted from the sodium-calcium-silicate system which had, for instance, a composition customary for window glasses.

The glass composition contained traces of refining agents and was not fully refined, so that it had residual contents of CO_2 , N_2 and H_2O . The temperature of the melt was about 1300 °C. A mesh situated in the glass melt and composed of Pt/10 Rh which had a refining electrode surface area of about 20 cm² served as refining electrode. A relatively large Pt/10 Rh surface area near the surface of the melt in the pot served as counter-electrode.

The refining electrode was connected anodically whilst the counter-electrode was connected cathodically. A direct voltage of 150 mV was applied to the electrodes as operating voltage, the voltage at the refining electrode being 150 mA. When the voltage was applied, oxygen bubbles formed at the refining electrode which had an average size of about 0.05 mm on leaving the electrode. The formation of the oxygen bubbles was observed

optically by means of a television camera and screen.

Under the refining conditions mentioned, about 2 bubbles per second were formed, the bubbles growing whilst moving upwards in the melt, i.e. their volume increasing. The uplift time in the melt for one bubble was about 2 hours. The analysis of the bubbles after rising gave a content per bubble of a maximum of 50% CO_2 and 30% N_2 at the beginning of electrolytic refining, these proportions decreasing as refining of the glass melt progressed.

It could thus be shown with this test carried out on a laboratory scale that glass melts may be refined electrochemically by means of direct voltage. In the pot test the melt was stationary, in contrast to the flowing melts present on an industrial scale, but the results can be transferred by the man skilled in the art to the conditions of flowing melts, in which a part of the oxygen evolved at the electrode is removed without participating in bubble formation.

Example B:

In an assembly of the apparatus similar to example A, a glass melt the same as in example A was refined by applying an alternating voltage of 1 V and 5 to the electrodes as operating voltage. A direct voltage of 100 mV is then produced in the case of alternating current. The alternating current at the refining electrode was eventually 20 A, a direct current of +200 mA being produced.

Except for the differences in the numerical values of voltage and current, the refining results were identical.

Claims

1. A process for refining an oxide melt, in which a refining gas is generated electrochemically in situ in the oxide melt, wherein the refining gas is oxygen.
2. A process according to claim 1, wherein the refining gas is generated using at least two electrodes including a refining electrode and a counter-electrode, which are both in contact at least partially with the oxide melt, wherein a voltage is applied to the electrodes, and oxygen is evolved at one or more of the electrodes as refining gas for the removal of unwanted gases from the oxide melt.
3. A process according to claim 2, wherein the refining electrode is provided completely inside the oxide melt, and the counter-electrode is partially immersed in the oxide melt and is partially in contact with the atmosphere above the oxide layer.
4. A process according to claim 3, wherein the oxide melt is melted in a melting unit, and the refining electrode is provided on or adjacent the bottom of the melting unit.
5. A process according to any one of claims 2 to 4, wherein a dc voltage is applied to the electrodes from a power source, the refining electrode being in contact with the positive pole and the counter-electrode being in contact with the negative pole of the power source.
6. A process according to any one of claims 2 to 4,

wherein an ac voltage is applied to the electrodes, and the electrodes have different surface areas.

7. A process according to claim 6, wherein the current density is greater at the refining electrode than at the counter-electrode.
8. A process according to claim 6 or 7, wherein a dc voltage is superimposed on an ac voltage.
9. A process according to any preceding claim, wherein the voltage applied to both the electrodes is adjustable.
10. A process according to claim 9, wherein the voltage is adjusted electrically or with a resistor, as a result of which the size of the oxygen bubbles evolved can be adjusted.
11. A process according to any one of claims 3 to 10, wherein the atmosphere above the oxide melt with which the counter-electrode is in contact contains enough oxygen to prevent electrolytic decomposition of the oxide melt when the voltage is applied.
12. A process according to any preceding claim, wherein a redox refining agent is added to the melt for the resorption of residual refining bubbles.
13. An oxide melt when refined by a process as claimed in any preceding claim.
14. An oxide melt as claimed in claim 13, which is a glass melt.

15. A glass article when produced from an oxide melt as claimed in claim 14.

Relevant Technical fields

(i) UK CI (Edition L) C1M (MDD)

(ii) Int CI (Edition 5) C03B

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Search Examiner

V V BAILEY-WOOD

Date of Search

23 APRIL 1993

Documents considered relevant following a search in respect of claims 1-15

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).